PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
A01N 47/02, 43/56, A61K 31/415 // (A01N 47/02, 47:34) (A01N 43/56, 47:34) (A61K 31/415, 31:17)

A1

(11) International Publication Number: **WO 98/39972**

(43) International Publication Date: 17 September 1998 (17.09.98)

(21) International Application Number: PCT/EP98/01224

(22) International Filing Date: 5 March 1998 (05.03.98)

(30) Priority Data:

08/815,429	11 March 1997 (11.03.97)	US
60/054,795	5 August 1997 (05.08.97)	US

(71) Applicant *(for all designated States except US)*: RHONE-POULENC AGRO [FR/FR]; 14-20, rue Pierre Baizet, F-69009 Lyon (FR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: HAAS, Charles, Lee [US/US]; 702 Buckingham Road, Garner, NC 27529 (US). PILATO, Michael [US/US]; 206 Livingstone Drive, Cary, NC 27513 (US). TIMMONS, Philip, Reid [US/US]; 4423 Dula Street, Durham, NC 27705 (US). WU, Tai-Teh [US/US]; 200 Collinson Drive, Chapel Hill, NC 27514 (US). HUBER, Scot, Kevin [US/US]; 7409 Wisconsin Court, Raleigh, NC 27615 (US). LEROUX, Bernard [FR/US]; 2320 Weybridge Drive, Raleigh, NC 27615 (US).

(74) Agent: BRACHOTTE, Charles; Rhône-Poulenc Agro, Boîte postale 9163, F-69263 Lyon Cedex 09 (FR).

(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, GW, HU, ID, IL, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

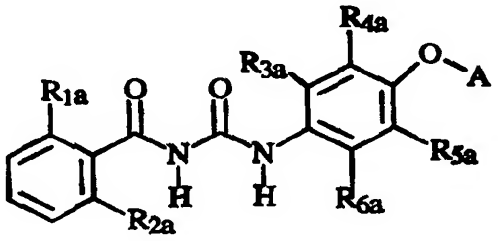
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

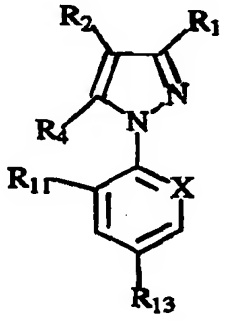
(54) Title: PESTICIDAL COMBINATION

(57) Abstract

A pesticidal combination comprising a compound of formula (I) and a 1-arylpyrazole of formula (II).



(I)



(II)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

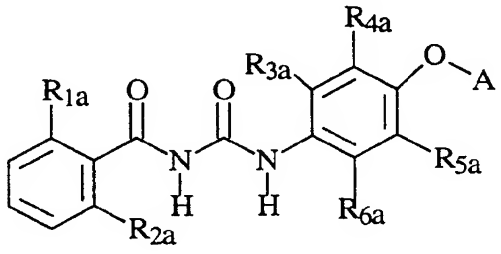
AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

Pesticidal Combination

The present invention relates to a new pesticidal combination, a composition comprising the combination and to a method of controlling pests. The invention further relates to a process for the preparation of the novel composition, to the use thereof and to plant propagation material treated therewith, and to the use of a compound of formula (I) below for the preparation of said novel composition.

Certain mixtures of pesticides have been proposed in the literature for pest control. However, the biological properties of these known mixtures are unable to satisfy the requirements made of them in the field of pest control in all respects, so that there is still a need to provide further mixtures having synergistic properties for pest control, in particular for controlling insects and representatives of the orders. In particular, the problem in the control of pests in animals is the necessity to provide repeated doses in an animal over a short time period. Such repeated dosing exposes the animal owner or keeper to the pesticide. Thus there exists a need to provide more long-lasting pesticidal treatments, preferably with doses of pesticide at or below those generally used in the art. This need is met in whole or in part by the provisions of this invention.

Accordingly, the invention relates to a pesticidal combination comprising a compound of formula (I):



(I)

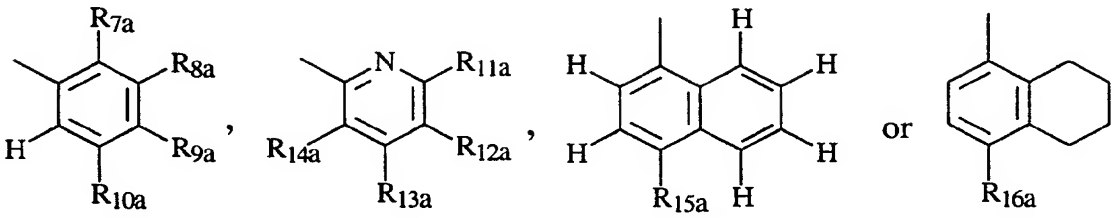
wherein:

R_{1a} and R_{2a} are independent of one another, hydrogen or halogen;

R_{3a} is hydrogen, chlorine or alkyl;

R_{4a}, R_{5a} and R_{6a} are independent of one another, alkyl, preferably methyl hydrogen, or halogen;

A is G1, G2, G3 or G4:

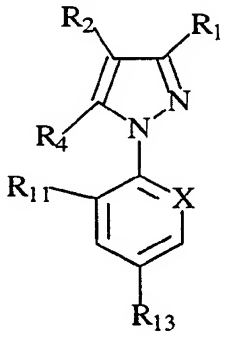


(G1) (G2) (G3) (G4)

wherein R_{7a} to R_{16a} are independent of one another, hydrogen, halogen, alkyl or nitro; and

provided that R_{1a} and R_{2a} are not simultaneously hydrogen; and that R_{4a}, R_{5a} and R_{6a} are not simultaneously hydrogen;

in the free form or in the form of a pesticidally acceptable salt thereof, and a 1-arylpyrazole of formula (II):



(II)

wherein:

R_1 is CN or methyl;

R_2 is $S(O)_nR_3$;

R_3 is alkyl or haloalkyl;

R_4 is selected from the group consisting of hydrogen, halogen,

$-NR_5R_6$, $-C(O)OR_7$, $-S(O)_mR_7$, alkyl, haloalkyl, $-OR_8$,

$-N=C(R_9)(R_{10})$ and -C(O)alkyl;

R_5 and R_6 are independently selected from a hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, -C(O)OR_7, -$S(O)_rCF_3$; or R_5 and R_6 form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_7 is selected from alkyl and haloalkyl;

R_8 is selected from alkyl, haloalkyl and hydrogen;

R_9 is selected from hydrogen and alkyl;

R_{10} is selected from phenyl or heteroaryl each of which is optionally substituted by one or more hydroxy, halogen, -O-alkyl, -S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from nitrogen and C-R_{12};

R_{11} and R_{12} are independently selected from halogen or hydrogen;

R_{13} is selected from halogen, haloalkyl, haloalkoxy, -$S(O)_qCF_3$, -SF_5;

m, n, q, r are independently selected from 0, 1, and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3, and X is N.

The alkyl groups of formula (I) are optionally substituted by one or more halogens.

The alkyl and alkoxy groups and moieties of the formula (II) are preferably lower alkyl and alkoxy groups, that is, groups having one to four carbon atoms. The haloalkyl and haloalkoxy groups likewise preferably have one to four carbon atoms. The haloalkyl and haloalkoxy groups can bear one or more halogen atoms; preferred groups of this type include -CF_3 and -OCF_3. It shall be understood that the ring formed by the divalent alkylene radical represented by R_5 and R_6 and including the nitrogen atom to which R_5 and R_6 are attached is generally a 5, 6, or 7-membered ring. It will be understood that the compounds of formula (I) and the 1-phenylpyrazoles of formula (II) include enantiomers and/or diastereomers thereof. The invention embraces these and mixtures thereof.

A preferred group of compounds of formula (I) for use in the present invention are those with one or more of the following features wherein

R_{1a} and R_{2a} are independently selected from halogen, preferably chlorine or fluorine;

A is G1;

R_{3a} is methyl;

R_{4a}, R_{5a} and R_{6a} are independently hydrogen, halogen, preferably chlorine, or methyl; or

R_{7a}, R_{8a}, R_{9a} and R_{10a} are independently selected from hydrogen or halogen.

A preferred group of 1-arylpyrazoles for use in the present invention are those of formula (II) with one or more of the following features wherein:

R_1 is CN;

R_4 is $-NR_5R_6$;

R_5 and R_6 are independently selected from the hydrogen atom, alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$;

X is $C-R_{12}$; or

R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy, and $-SF_5$.

A particularly preferred group of 1 -arylpyrazoles for use in the present invention are those of formula (II) wherein:

R_1 is CN;

R_4 is $-NR_5R_6$;

R_5 and R_6 are independently selected from the hydrogen atom, alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$;

X is $C-R_{12}$; and

R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy, and $-SF_5$.

According to the present invention a very particularly preferred compound of formula (II) is 5-amino-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile, known as fipronil.

A preferred combination is that of a compound of formula (I) and a 1-arylpyrazole of formula (II) wherein R_1 is CN, R_2 is -S(O)Et, R_{11} is Cl, X is C-Cl, R_{13} is CF_3 and R_4 is selected from $-NH_2$, -NHMe or -NHEt, particularly 5-amino-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-ethylsulfinylpyrazole-3-carbonitrile also known as Compound B.

A particularly preferred combination is that of a compound of formula (I) wherein R_{1a}=R_{2a}=F; R_{3a}=R_{5a}=Me; R_{4a}=Cl; R_{6a}=H; A=G1; R_{7a}=R_{9a}=Cl; R_{8a}=R_{10a}=H, also called 1-[4-(2,4-dichlorophenoxy)-2,5-dimethyl-3-chlorophenyl]-3-(2,6-difluorobenzoyl)urea, hereinafter known as Compound (C); and a compound of formula (II).

The general preparation of compounds of formula (I) may be found in U.S. Patent 5,135,953 and references recited therein.

The preparation of compounds of formula (II) is described in International Patent Publications No. WO 87/03781, WO 93/06089 and WO 94/21606, as well as in European Patent Publication numbers 0295117, 0403300, 0385809, and 0679650, German Patent Publication 19511269 and United States Patents 5,232,940 and 5,236,938.

The pesticidally acceptable salts of the compound of formula (I) are typically addition salts of inorganic and organic acids, preferably of hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, perchloric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, oxalic acid, malonic acid, toluenesulfonic acid or benzoic acid.

Preferred combinations within the scope of this invention are those that contain the compound of formula (I) in the free form as an active ingredient.

A combination of the compound of formula (I) and only one 1-arylpyrazole of formula (II) is also preferred.

Other compounds of formula (I) which may be used in the present invention are those listed in Table (I).

Table 1

Cmpd. No.	R_{1a}	R_{2a}	R_{3a}	R_{4a}	R_{5a}	R_{6a}	A	R_{7a}	R_{8a}	R_{9a}	R_{10a}	R_{11a}	R_{12a}	R_{13a}	R_{14a}	R_{15a}
1	F	F	H	Cl	Cl	H	G2	--	--	--	--	H	CF_3	H	Cl	--
2	F	F	H	Cl	Cl	H	G1	H	H	NO_2	H	--	--	--	--	--
3	F	F	H	Cl	Cl	H	G3	--	--	--	--	--	--	--	--	Cl
4	F	F	H	H	CF_3	H	G3	--	--	--	--	--	--	--	--	Cl
5	F	F	H	H	CH_3	H	G3	--	--	--	--	--	--	--	--	Cl
6	F	F	H	H	H	H	G3	--	--	--	--	--	--	--	--	Cl
7	F	F	CH_3	H	CH_3	H	G3	--	--	--	--	--	--	--	--	Cl
8	H	Cl	CH_3	Cl	CH_3	H	G3	--	--	--	--	--	--	--	--	Cl
9	F	F	H	Cl	Cl	H	G2	--	--	--	--	H	Cl	H	Cl	--
10	F	F	CH_3	H	Cl	H	G3	--	--	--	--	--	--	--	--	Cl
11	Cl	H	CH_3	Cl	CH_3	H	G1	CH_3	H	CH_3	H	--	--	--	--	--
12	F	F	CH_3	Cl	CH_3	H	G1	CH_3	H	Cl	CH_3	--	--	--	--	--
13	F	F	CH_3	Cl	CH_3	H	G1	CH_3	CH_3	Br	H	--	--	--	--	--
14	F	F	H	Cl	Cl	H	G1	H	H	Cl	H	--	--	--	--	--
15	F	F	CH_3	Cl	CH_3	H	G1	Cl	H	Cl	H	--	--	--	--	--
16	F	F	Cl	Cl	H	Cl	G3	--	--	--	--	--	--	--	--	Cl
17	F	H	CH_3	Cl	CH_3	H	G1	Br	H	Cl	H	--	--	--	--	--
18	F	F	CH_3	Cl	CF_2H	H	G3	--	--	--	--	--	--	--	--	Cl
19	F	F	CH_3	Cl	CH_3	H	G3	--	--	--	--	--	--	--	--	Cl

The pesticidal combination of this invention will preferably contain compound of formula (I) and 1-arylpyrazole in a weight ratio of 1:50 to 50:1, especially in a ratio from 1:20 to 20:1, more particularly from 10:1 to 1:10, still more particularly from 5:1 to 1:5, very particularly from 2:1 to 1:2, for example in the ratio 1:1.

The combination of the pesticide of formula (I) and the 1-arylpyrazoles of formula (II) provides a generally long acting effect, generally from 30 to 180 days, preferably from 180 to 240 days, more preferably from 240 to 300, and most preferably from 300 to 360 days after treatment. An additive enhancement of the activity spectrum on the pests to be controlled can also be obtained. The combination can also provide a synergistic effect that potentiates the activity ranges of both compounds from two points of view.

On the one hand, the concentrations of the compound of formula (I) and the 1-arylpyrazoles of formula (II) are reduced with no reduction in the activity obtained. On the other hand, the combination also achieves a high degree of pest control where the individual compounds are substantially or completely inactive at low concentrations. This feature permits on the one hand a broadening of the activity spectrum against the controllable pests and, on the other, an enhancement of safety of application.

The combinations of the invention also have a useful antifeeding effect. Such an antifeeding effect is generally not seen with the individual compounds of formula (I) or salts thereof. An antifeeding effect is advantageous in that regardless of the killing action of the active ingredients, the plant is protected from damage and therefore may provide effective protection to the locus so treated with the active ingredient.

The combinations of this invention have useful preventive and/or curative properties in the field of pest control even at low concentration. They are well tolerated by warm-blooded animals, fish and plants. and they have a very favorable biocidal spectrum. The compositions are effective against all, or individual, development stages of normally sensitive as well as resistant pests of animals such as insects and representatives of the order Acarina. The onset of the insecticidal and/or acaricidal action of the novel

compositions may follow directly, i.e.- a kill of the pests will occur immediately or only after some time. for example where moulting is effected. or indirectly, for example in diminished oviposition and/or hatching rate.

The mixtures of the invention are most valuable by their long term effect as well as by their good margin of safety for veterinary and nuisance insect applications. They are also most useful because of their combined activity on parasites, preferably both ticks and fleas, especially those of pets, such as dogs or cats, particularly cats. The combination of the compounds of formula (II) with a compound of formula (I), especially compound (C), therefore generally provides a solution to the problem of flea and tick control.

Generally, one administration per week, preferably one administration per month, more preferably one administration every two to three months, even more preferably one administration every four to six months, even more preferably one administration every seven to eight months, and most preferably every nine to twelve months or higher provide generally good efficacy.

Another advantage of the combination of the invention is that it is well adapted to oral administration or administration by injection, particularly subcutaneous injection or by subcutaneous implant which methods are generally known to those skilled in the art. The appropriate doses are generally from 5 to 50 mg/kg, preferably 10 to 30 mg/kg for the compound of formula (II), "mg/kg" in this instance indicating the milligrams of compound of formula (II) per kilogram of body weight of animal. The amount the compound of formula (I) compound present in the mixture will vary according to the efficacy the active ingredient and the precise conditions of use and is generally from 1 to 100 mg/kg, preferably from 5 to 80 mg/kg, more preferably from 10 to 50 mg/kg, and most preferably from 10 to 20 mg/ kg..

The term “parasites” as used in the specification and claims is meant to encompass all endoparasites and ectoparasites of warm-blooded animals as well as pests that breed in the manure of the animals.

The aforementioned animal pests typically include:

of the order Lepidoptera

Acleris spp., Adoxophyes spp., Aegeria spp., Agrotis spp., Alabama argulaceae, Amylois spp., Anticarsia gemmatalis, Archips spp., Argyrotaenia spp., Autographa spp., Busseola fusca, Cadra cautella. Carposina nipponensis, Chilo spp., Choristoneura spp., Clysia ambigueua, Cnaphalocrocis spp., Cnephasia spp., Cochylis spp., Coleophora spp., Crocidolomia binotaus, Cryptophlebia leucotreta, Cydia spp., Diatraea spp., Diparopsis castanea, Earias spp., Ephestia spp., Eucosma spp., Eupoecilia ambiguena, Euproctis spp., Euxoa spp.. Grapholita spp., Hedya nubiferana, Heliothis spp., Hellula andalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella. Lithocllethis spp., Lobesia botrana, Lymantria spp., Lyonetia spp., Malacosoma spp., Mamestra brassicae, Manduca sexta, Operophtera spp., Ostrinia nubilalis, Pammene spp., Pandemis spp., Panolis flammea, Pectinophora gossypieua, Phthorimaea operculeua, Pieris rapae, Pieris spp., Plutella xylostella. Prays spp., Scirpophaga spp., Sesamia spp., Sparganothis spp., Spodoptera spp.. Synanthedon spp., Thaumetopoea spp., Tortrix spp., Trichoplusia ni and Yponomeuta spp.;

of the order Coleoptera, for example

Agriotes spp., Anthonomus spp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites spp., Curculio spp., Dermestes spp., Diabrotica spp., Epilachna spp., Eremnus spp., Leptinotarsa decemlineata, Lissorhoptrus spp., Melolontha spp., Oryzaephilus spp., Otiorhynchus spp., Phlyctinus spp., Popillia spp., Psylliodes spp., Rhizopertha spp., Scarabeidae, Sitophilus spp., Sitotroga spp., Tenebrio spp., Tribolium spp. and Trogoderma spp.;

of the order Orthoptera., for example

Blatta spp., Blattella spp., Gryllotalpa spp., Leucophaea maderae, Locusta spp., Periplaneta spp. and Schistocerca spp.;

of the order Isoptera, for example

Reticulitermes spp.;

of the order Psocoptera, for example

Liposcelis spp.;

of the order Anoplura, for example

Haematopinus spp., Linognathus spp., Pediculus spp., Pemphigus spp. and Phylloxera spp.;

of the order Mallophaga, for example

Damalinea spp. and Trichodectes spp.;

of the order Thysanoptera, for example

Frankliniella spp., Hercinothrips spp., Taeniothrips spp., Thrips palmi, Thrips tabaci and Scirtothrips aurantii;

of the order Heteroptera, for example

Cimex spp., Distantiella theobroma, Dysdercus spp., Euchistus spp. Eurygaster spp., Leptocorisa spp.. Nezara spp., Piesma spp., Rhodnius spp., Sahlbergella singularis, Scotinophara spp. and Triatoma spp.;

of the order Homoptera, for example

Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella spp., Aphididae, Aphis spp., Aspidiotus spp., Bemisia tabaci, Ceroplaster spp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Coccus hesperidum. Empoasca spp., Eriosoma lanigerum, Erythroneura spp.. Gascardia spp., Laodelphax spp., Lecanium corni. Lepidosaphes spp., Macrosiphus spp., Myzus spp.. Nephotettix spp., Nilaparvata spp., Paratoria spp., Pemphigus spp., Planococcus spp., Pseudaulacaspis spp.. Pseudococcus spp., Psylia spp., Pulvinaria aethiopica, Quadraspidiotus spp., Rhopalosiphum spp., Saissetia spp., Scaphoideus spp., Schizaphis spp., Sitobion spp., Trialeurodes vaporariorum, Trioza erytreae and Unaspis citri;

of the order Hymenoptera, for example

Acromyrmex, Atta spp., Cephus spp., Diprion spp., Diprionidae, Gilpinia polytoma, Hoplocampa spp., Lasius spp., Monomorium pharaonis, Neodiprion spp., Solenopsis spp. and Vespa spp.;

of the order Diptera. for exarnple

Aedes spp.. Antherigona soccata, Bibio hortulanus, Calliphora erythrocephala, Ceratitis spp., Chrysomyia spp., Culex spp., Cuterebra spp., Dacus spp., Drosophila melanogaster, Fannia spp., Gastrophilus spp., Glossina spp., Hypoderma spp., Hyppobosca spp.,

Liriomyza spp., Lucilia spp., Melanagromyza spp., Musca spp.. Oestrus spp., Orseolia spp., Oscinella frit, Pegomyia hyoscyami , Phorbia spp., Rhagoletis pomonella, Sciara spp., Stomoxys spp., Tabanus spp., Tannia spp. and Tipula spp.;
of the order Siphonaptera for example
Ceratophyllus spp. and Xenopsylla cheopis;
of the order Thysanura, for example
Lepisma saccharina and
of the order Acarina. for example
Acarus siro, Aceria sheldoni, Aculus schlechtendali, Amblyomma spp., Argas spp., Boophilus spp., Brevipalpus spp., Bryobia praetiosa, Calipitrimerus spp., Chorioptes spp., Dermanyssus gallinae, Eotetranychus carpini, Eriophyes spp., Hyalomma spp., Ixodes spp., Olygonychus pratensis, Ornithodoros spp., Panonychus spp., Phyllocoptrum oleivora, Polyphagotarsonemus latus, Psoroptes spp.. Rhipicephalus spp., Rhizoglyphus spp.. Sarcoptes spp., Tarsonemus spp. and Tetranychus spp.

Within the scope of this invention it is possible to control in particular pests:

(1) of the order Lepidoptera, especially Adoxophyes spp.. Alabama argillaceae, Clysia ambigulla, Clysia pomonelia, Crocidolomia binotalis, Cydia spp., Earias spp., Heliothis spp.. Lobesia botrana, Ostrinia nubilalis, Phthohmea operculeua, Sparganothis spp. and Spodoptera spp.;

(2) of the order Coleoptera, in particular the family Curculionidae, more particularly Anthonomus spp., more particularly still A. grandis, very particularly the family Chrysomelidae, most preferably Leptinotarsa decemlineata;

(3) of the order Homoptera, in particular the family Aphididae, more particularly the genus Aphis, most particularly A. gossypii; in particular the family Aleurodidae, preferably Aleurothrixus floccus and Bemisia tabaci; in particular Fainilie Psyllidae, more preferably Psylla spp.,

(4) of the order Thysanoptera, in particular the family Thripidae, preferably Frankliniella spp., Thrips palmi and Thrips tabaci;

(5) of the order Acarina, in particular the family Eriophyidae, more particularly Aculus schlechtendali and Phyllocoptruta oleivora;

(6) of the order Diptera, in particular the family Agromyzidae, more particularly Liriomyza trifolii;

(7) of the order Isoptera, Reticulitermes spp.

(8) of the order Orthoptera, Blattella spp. and Periplaneta spp.

Preferably, representative parasites which may be controlled by the method of this invention include members of the Arthropoda (Arthropods), including mites in suborder Mesostigmata, Sarcoptiformes, Trombidiformes and Onchychopalpida; sucking and biting lice in orders Anoplura and Mallophaga; ticks in the families Ixodidac and Argasidae; fleas in the families Pulicidae, Ceratophyllidae, and others; Cimex and other Hemiptera; Triatominae and other Heteroptera; and myiasis-related fly larvae and blood sucking adults (including mosquitoes) in the suborders Brachycera, Cyclorrhapha and Nematocera. Representative also are helminths included in the Nematoda (Strongylidia, including but not limited to Strongyloidea, Ancylostomatoidea, Trichostrongyloidea and Metastrongyloidea; Ascarida [Ascaris]; Filariina, such as but not limited to Onchocerca and Dirofilaria; Rhabditida; and trichinellida); Cestoidea, especially Cyclophyllidea, and Trematoda, including Strigeatoidea such as Schistosoma; Echinostomida such as Fasciola; and Plagiorchiida such as Paragonimus. Other parasites which may be controlled by compounds represented by generic formula (I) include Acanthocephala such as Macracanthorhynchus or Moniliformis, and Pentastomida, especially Liguatula; and protozoa, especially Coccidia such as Eimeria and Plasmodium, Piroplasmea such as

Babesia; Toxoplasmea such as Tripanosoma; Trichomonadidae such as Trichomonas and Entamoebidae such as Entamoeba.

Illustrative of specific parasites of various host animals which may be controlled by the method of this invention include arthropods such as mites (mesostigmatids, itch, mange, scabies, chiggers), ticks (soft-bodied and hard-bodied), lice (sucking, biting), fleas (dog flea, cat flea, oriental rat flea, human flea), true bugs (bed bugs, Triatomid bugs), bloodsucking adult flies (horn fly, horse fly, stable fly, black fly, deer fly, louse fly, tsetse fly, mosquitoes), and parasitic fly maggots 9bot fly, blow fly, screwworm, cattle grub, fleeceworm); helminths such as nematodes (threadworm, lungworm, hookworm, whipworm, nodular worm, stomach worm, round worm, pinworm, heartworm), cestodes (tapeworms) and trematodes (liver fluke, blood fluke); protozoa such as coccidia, trypanosomes, trichmonads, amoebas and plasmodia; acanthocephalans such as throny-headed worms (lingulatulida); and pentastomids such as tongueworms.

With the novel pesticidal combinations it is possible to control, i.e. inhibit or destroy, in particular pests of the above mentioned type that occur in plants, especially. in cultivated plants and ornamentals, in horticulture and in forestry, or in parts of such plants as fruit, blossoms, leaves, stems, tubers or roots, while in some cases parts of plants that grow later can also be protected against these pests.

The pesticidal combination of this invention can be used with advantage for pest control in cereals such as maize or sorghum; fruit such as pome fruit, stone fruit and soft fruit, typically apples, pears, plums, peaches. almonds, cherries, or berries, for example strawberries, raspberries and blackberries; leguminous plants, typically including beans, lentils, peas and soybeans, oil plants such as rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans and groundnuts; cucurbits such as marrows, cucumber and melons; fibre plants such as cotton, flax. hemp and jute; citrus fruit such as oranges, lemons, grapefruit and mandarins; vegetables such as spinach. lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; lauraceae such as avocados, cinnamon and camphor, and tobacco, nuts, coffee, egg plants, sugar cane, tea,

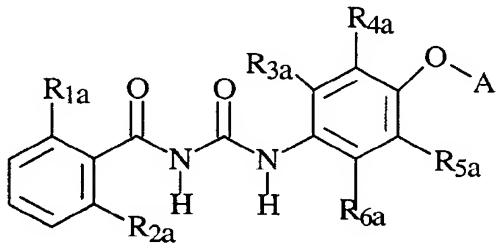
pepper, vines, hops, bananas and natural rubber plants or ornamentals, in particular in maize, sorghum, pome fruit, stone fruit. leguminous plants, cucurbits. cotton. citrus fruit, vegetables, egg plants. vines, hops or ornamentals; preferably in maize, sorghum, apples, pears, plums, peaches, peas. soybeans, olives, sunflowers, coconuts, cocoa beans, cabbages, tomatoes, potatoes, vines or cotton; and, most preferably, in vines. citrus fruit, apples. pears, tomatoes and cotton.

Further utilities of the pesticidal combinations of this invention are the protection of stored goods and materials as well as in the hygiene sector, for example, domestic animals and productive livestock against pests of the indicated type.

The method of the present invention comprises known methods of application of the compound of the invention to the domestic animal including spraying, rubbing, application by spotting, dip, collar, ear tag, or orally. Preferably the compounds of the invention are administered orally (that is into the digestive tract) or via injection. Most preferably the compounds are administered orally via a bolus.

According to the present invention, the frequency of treatment of the domestic animal to be treated by the compound of formula (I) is generally from about once per week to about once per year, preferably from about once every two weeks to about once every six months, and most preferably from about once per month to about once every three months.

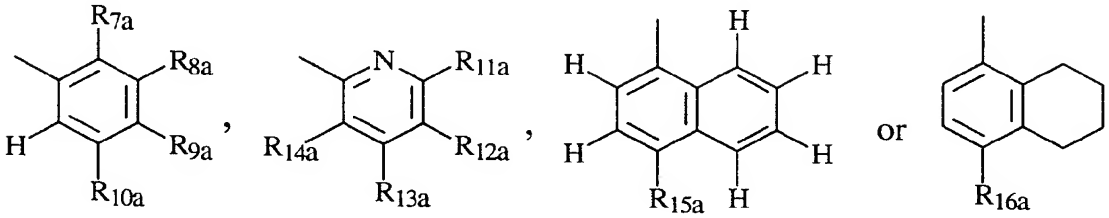
The present invention also relates to a use of a combination comprising a compound of formula (I)



R_{3a} is hydrogen, chlorine or alkyl;

R_{4a}, R_{5a} and R_{6a} are independent of one another, alkyl, preferably methyl hydrogen, or halogen;

A is G1, G2, G3 or G4:

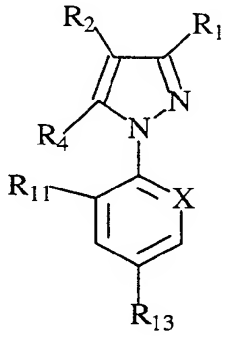


(G1) (G2) (G3) (G4)

wherein R_{7a} to R_{16a} are independent of one another, hydrogen, halogen, alkyl or nitro; and

provided that R_{1a} and R_{2a} are not simultaneously hydrogen; and that R_{4a}, R_{5a} and R_{6a} are not simultaneously hydrogen;

in the free form or in the form of a pesticidally acceptable salt thereof, and a 1-arylpyrazole of formula (II):



(II)

wherein:

R_1 is CN or methyl;

R_2 is $S(O)_nR_3$;

R_3 is alkyl or haloalkyl;

R_4 is selected from the group consisting of hydrogen, halogen, $-NR_5R_6$, $-C(O)OR_7$, $-S(O)_mR_7$, alkyl, haloalkyl, $-OR_8$, $-N=C(R_9)(R_{10})$ and -C(O)alkyl;

R_5 and R_6 are independently selected from a hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, $-C(O)OR_7$, $-S(O)_rCF_3$; or R_5 and R_6 form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_7 is selected from alkyl and haloalkyl;

R_8 is selected from alkyl, haloalkyl and hydrogen;

R_9 is selected from hydrogen and alkyl;

R_{10} is selected from phenyl or heteroaryl each of which is optionally substituted by one or more hydroxy, halogen, -O-alkyl, -S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from nitrogen and C-R_{12};

R_{11} and R_{12} are independently selected from halogen or hydrogen;

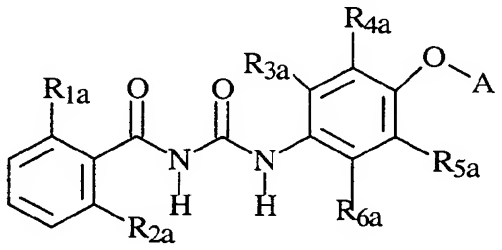
R_{13} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_qCF_3$, $-SF_5$;

m, n, q, r are independently selected from 0, 1, and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3, and X is N;

to manufacture a composition for the control of parasites in or on an animal.

The present invention also relates to a method of cleaning animals in good health comprising the application to the animal of a combination of a compound or formula (I):

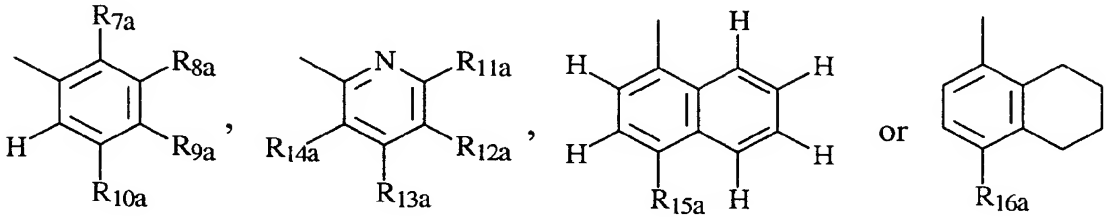


wherein

R_{3a} is hydrogen, chlorine or alkyl;

R_{4a}, R_{5a} and R_{6a} are independent of one another, alkyl, preferably methyl hydrogen, or halogen;

A is G1, G2, G3 or G4:

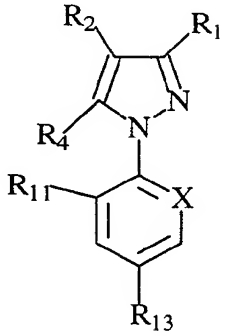


(G1) (G2) (G3) (G4)

wherein R_{7a} to R_{16a} are independent of one another, hydrogen, halogen, alkyl or nitro; and

provided that R_{1a} and R_{2a} are not simultaneously hydrogen; and that R_{4a}, R_{5a} and R_{6a} are not simultaneously hydrogen;

in the free form or in the form of a pesticidally acceptable salt thereof, and a 1-arylpyrazole of formula (II):



(II)

wherein:

R_1 is CN or methyl;

R_2 is $S(O)_nR_3$;

R_3 is alkyl or haloalkyl;

R_4 is selected from the group consisting of hydrogen, halogen, $-NR_5R_6$, $-C(O)OR_7$, $-S(O)_mR_7$, alkyl, haloalkyl, $-OR_8$, $-N=C(R_9)(R_{10})$ and -C(O)alkyl;

R_5 and R_6 are independently selected from a hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, $-C(O)OR_7$, $-S(O)_rCF_3$; or R_5 and R_6 form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_7 is selected from alkyl and haloalkyl;

R_8 is selected from alkyl, haloalkyl and hydrogen;

R_9 is selected from hydrogen and alkyl;

R_{10} is selected from phenyl or heteroaryl each of which is optionally substituted by one or more hydroxy, halogen, -O-alkyl, -S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from nitrogen and C-R_{12};

R_{11} and R_{12} are independently selected from halogen or hydrogen;

R_{13} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_qCF_3$, $-SF_5$;

m, n, q, r are independently selected from 0, 1, and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3, and X is N;

or a composition comprising the combination to the animal.

The method of cleaning an animal is not a method of treatment of the animal body per se, because

(a) the animal is in good health and requires no substantial treatment to correct a deficiency of health;

(b) the cleaning of the animal is not intended to be done by veterinary personnel, but by persons interested in the cleaning of the animal; and

(c) the purpose of such cleaning is to avoid unpleasant conditions for humans and the environment in which humans inhabit so as to not infest the said humans with arthropods carried by the animal.

The present invention also relates to a composition comprising an arthropocidally effective, substantially non-emetic amount of a compound of formula (I) and an acceptable carrier. Acceptable carriers acceptable for the use of the compounds are generally known to the skilled addressee concerned with arthropod control in animals, particularly domestic animals.

A particularly advantageous utility of the instant invention is in the protection of structures from nuisance insects including termites and cockroaches and ants.

The invention also relates to compositions comprising a combination of a compound of formula (I) and the 1-arylpyrazole of formula (II) in association with a pesticidally acceptable adjuvant.

Depending on the intended objectives and the prevailing circumstances, the pesticidal compositions are generally emulsifiable concentrates. suspension concentrates. directly sprayable or dilutable solutions, coatable pastes, dilute emulsions, wettable powders, soluble powders, dispersible powders, wettable powders, dusts, granulates or encapsulations in polymer substances, comprising a compound of formula (I) and a 1-arylpyrazole of formula (II).

The active ingredients are generally used in those compositions in pure form, the solid compounds being typically used in a specific particle size, or preferably together with at least one of the adjuvants customary in formulation technology, for example extenders such as solvents, or solid carriers, or surface-active compounds (surfactants).

Suitable solvents are typically aromatic hydrocarbons or partially hydrogenated aromatic hydrocarbons, preferably the fraction of alkylbenzenes containing 8 to 12 carbon atoms,

such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons such as paraffins or cyclohexane; alcohols such as ethanol, propanol or butanol; glycols and their ethers and esters such as propylene glycol dipropylene glycol ether, diethylene glycol or 2-methoxyethanol or 2-ethoxyethanol; ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide; water, vegetable oils or epoxidised vegetable oils such as rape oil, castor oil. coconut oil or soybean oil or epoxidised rape oil, castor oil, coconut oil or soybean oil, and silicone oils.

The solid carriers typically used for dusts and dispersible powders are usually natural mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. To improve the physical properties it is also possible to add highly dispersed silicic acids or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types. including pumice, broken brick, sepiolite or bentonite, and suitable nonsorbent carriers are calcite or sand. In addition, innumerable granulated materials of inorganic or organic nature may be used, especially dolomite or pulverized plant residues.

Another type of solid carrier that may be used in the present invention is a biodegradable polymer, particularly one which degrades inside the animal's body over an extended period of time, preferably one administration per month, more preferably two to three months, even more preferably four to six months, much more preferably seven to eight months, and most preferably nine to twelve months.

Depending on the type of compound to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants or mixtures of surfactants preferably having good emulsifying, dispersing and wetting properties. The surfactants listed below shall be regarded merely as exemplary; many more surfactants customarily employed in formulation technology and suitable for use in the practice of the invention are described in the relevant literature.

Nonionic surfactants are preferably polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, said derivatives containing 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety and 6 to 18 carbon atoms in the alkyl moiety of the alkylphenols. Further suitable nonionic surfactants are water-soluble polyadducts of polyethylene oxide with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol containing 1 to 10 carbon atoms in the alkyl chain, which adducts contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. These compounds usually contain 1 to 5 ethylene glycol units per propylene glycol unit. Representative examples of nonionic surfactants are nonylphenol polyethoxyethanols, polyethoxylated castor oil, polyadducts of polypropylene and polyethylene oxide, tributylphenol polyethoxylate, polyethylene glycol and octylphenol polyethoxylate. Fatty acid esters of polyoxyethylene sorbitan, e.g. polyoxyethylene sorbitan trioleate, are also suitable nonionic surfactants.

Cationic surfactants are preferably quaternary ammonium salts carrying, as N-substituent, at least one C_8-C_{22} alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates. Examples are stearyldimethylammonium chloride and benzyl bis(2-chloroethyl)ethylammonium bromide.

Suitable anionic surfactants may be water-soluble soaps as well as water-soluble synthetic surface-active compounds. Suitable soaps are the alkali metal salts, alkaline earth metal salts and unsubstituted or substituted ammonium salts of higher fatty acids (C_{10}-C_{22}), e.g. the sodium or potassium salts of oleic or stearic acid or of natural fatty acid mixtures which can be obtained e.g. from coconut oil or tall oil. Further suitable soaps are also the fatty acid methyltaurine salts.

More frequently, however, synthetic surfactants are used, preferably fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty

sulfonates or sulfates are usually in the form of alkali metal salts, alkaline earth metal salts or unsubstituted or substituted ammonium salts and usually contain a C_8-C_{22} alkyl radical, which also includes the alkyl moiety of acyl radicals. Typical examples are the sodium or calcium salt of ligninsulfonic acid, of dodecyl sulfate or of a mixture of fatty alcohol sulfates obtained from natural fatty acids. These compounds also comprise the salts of sulfated and sulfonated fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain two sulfonic acid groups and one fatty acid radical containing 8 to 22 carbon atoms. Typical examples of alkylarylsulfonates are the sodium. calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, dibutylnaphthalenesulfonic acid or of a condensate of naphthalenesulfonic acid and formaldehyde. Corresponding phosphates, e.g. salts of the phosphoric acid ester of an adduct of p-nonylphenol with 4 to 14 mol of ethylene oxide, or phospholipids are also suitable.

The compositions will usually comprise 0.1 to 99 %. preferably 0.1 to 95% of a combination of the compound of formula (I) and one or more 1-arylpyrazoles of formula (II) and 1 to 99.9%, preferably 5 to 99.9%, of at least one solid or liquid adjuvant; usually they will contain 0 to 25%, preferably 0.1 to 20%, of surfactants (in each case percentages are by weight). Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations having a substantial lower concentration of active ingredient. Particularly preferred formulations will be made up as follows: (throughout, percentages are by weight):

<u>Emulsifiable concentrates:</u>

combination of (I) and (II):	1 to 95 %, preferably 5 to 20 %
surfactant:	1 to 30 preferably 10 to 20 %
solvent:	5 to 98 preferably 70 to 85 %

Dusts:	
combination of (I) and (II)	0.1 to 10, preferably 0.1 to 1%
solid carrier:	99.9 to 90%, preferably 99.9 to 99%
Suspension concentrates:	
combination of (I) and (II):	5 to 75%, preferably 10 to 50%
water:	94 to 24%, preferably 88 to 30%
surfactant:	1 to 40%, preferably 2 to 30%
Wettable powders:	
combination of (I) and (II):	0.5 to 90, preferably 1 to 80%
surfactant :	0.5 to 20, preferably 1 to 15%
solid carrier:	5 to 99, preferably 15 to 98%
Granules:	
combination of (I) and (II):	0.5 to 30, preferably 3 to 15%
solid carrier.	99.5 to 70%, preferably 97 to 85%

The novel compositions may also contain further solid or liquid adjuvants such as stabilizers, e.g. vegetable oils or epoxidised vegetable oils (e.g. epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, e.g. silicone oil, preservatives, viscosity regulators, binders and/or tackers, as well as fertilizers or other chemical agents for obtaining special effects, typically including bactericides, fungicides, nematicides, molluscicides or herbicides.

The compositions of this invention are prepared in known manner; in the absence of adjuvants, typically by grinding, sieving and/or compressing a solid active ingredient or mixture of active ingredients, for example to a specific particle size; and in the presence of at least one adjuvant, for example by intimately mixing and/or grinding the active ingredient or mixture of active ingredients with the adjuvant or adjuvants. The invention also relates to the preparation of the compositions.

The methods of applying the combinations, i.e. the methods of controlling pests at a locus of the indicated type, typically include spraying. atomizing, dusting, coating, dressing, scattering or pouring, selected in accordance with the intended objectives and prevailing circumstances, and the use of the combinations for controlling pests of the indicated type, are further objects of the invention. Typical rates of concentration are in the range from 0.01 to 1000 ppm, preferably from 0.1 to 500 ppm, of active ingredient. The rate of application may vary over a wide range and will depend on the nature of soil, the type of application (eg. foliar application, seed dressing application to the seed furrow), the cultivated plant, the pest to be controlled. the prevailing climatic conditions and other factors governed by the type of application, time of application and target crop. The rates of application per hectare will usually be from 0.5g/ha to 2000 g/ha, more particularly from 10 to 1000 g/ha, preferably from 20 to 600 g/ha.

A preferred method of application in the field of plant protection is application to the foliage of the plants (foliar application), the number of applications and the rate of application depending on the risk of infestation by the particular pest. However, the active ingredients can also penetrate the plants through the roots (systemic action) by drenching the locus of the plants with a liquid formulation or by applying the active ingredient in solid form to the locus of the plants, for example to the soil, e.g. in granular form (soil application). In paddy rice crops, such granules may be applied to the flooded rice field.

It is also contemplated that the invention comprises a compound of formula (I) in its free form or a pesticidally acceptable salt thereof and a 1-arylpyrazole of formula (II) for simultaneous, separate or sequential use in the control of pests at a locus.

The compositions of the invention are also suitable for protecting plant propagation material, e.g. seeds such as fruit, tubers or grains, or plant cuttings, against animal pests. The propagation material can be treated with the formulation before planting. Seeds, for example, can be dressed before sowing. The compounds of the invention can also be

applied to grains (eg. by coating), for example by impregnating the grains with a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the locus of planting when planting the propagation material, for example to the seed furrow during sowing. The invention relates also to these methods of treating plant propagation material and to the plant propagation material so treated.

The invention is illustrated by the following non-limiting Examples.

Formulation Examples (% = per cent by weight; ratios = weight ratios)

Example F1: Emulsifiable concentrate	a)	b)	c)
combination (ratio of compound of formula (I) to a compound (II) 1:1)	25	40 %	50 %
Ca dodecylbenzenesulfonate	5	8 %	6 %
polyethoxylated castor oil (36 mol EO)	5 %	-	-
tributylphenol polyethoxylate (30 mol EO)	-	12%	4%
cyclohexanone	-	15%	20%
xylene mixture	65 %	25%	20%

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

Example F2: Solutions	a)	b)	c)	d)
combination (2:1)	80%	10%	5%	95%
2-methoxyethanol	20%	-	-	-
polyethylene glycol MW 400	-	70%	-	-
N-methyl-2-pyrrolidone	-	20%	-	-
epoxidised coconut oil	-	-	1%	5%
petroleum spirit (boiling range 160-190°C)	-	-	94 %	-

The solutions are suitable for use in the form of microdrops.

Example F3- Granulates	a)	b)	c)	d)
combination (1:10)	5%	10%	8%	21%
kaolin	94%	-	79%	54%
highly dispersed silica	1%	-	13%	7%
attapulgite	-	90%	-	18%

The active ingredients are dissolved in dichloromethane, the solution is sprayed onto the carrier. and the solvent is subsequently evaporated in vacuo.

Example F4- Dusts	a)	b)
combination (1:5)	2%	5%
highly dispersed silica	1%	5%
talcum	97 %	-
kaolin	-	90%

Ready-to-use dusts are obtained by intimately mixing the carriers with the active ingredients.

Example F5: Wettable powders	a)	b)	c)
combination (1:1)	25%	50%	75%
sodium ligninsulfonate	5%	5%	-
sodium lauryl sulfate	3%	-	5%
sodium diisobutylnaphthalene-sulfonate	-	6%	10%
octylphenol polyethoxylate (7-8 mol EO)	-	2%	-
highly dispersed silica	5%	10%	10%
kaolin	62%	27%	-

The active ingredients are mixed with the additives, and the mixture is ground thoroughly in a suitable mill. This gives wettable powders which can be diluted with water to give suspensions of any desired concentrations.

Example F6: Emulsifiable concentrate	
combination (1:1)	10%
octylphenol polyethoxylate (4-5 mol EO)	3%
calcium dodecylbenzenesulfonate	3%
polyethoxylated castor oil (36 mol EO)	4%
cyclohexanone	30%
xylene mixture	50%

Emulsions of any desired concentration can be prepared from this concentrate by dilution with water.

Example F7: Dusts	a)	b)
combination (1:2)	5%	8%
talcum	95%	-
kaolin	-	92%

Ready-to-use dusts are obtained by mixing the active ingredients with the carrier and grinding the mixture on a suitable mill.

Example F8: Extruder granules

combination (1:3)	10%
sodium ligninsulfonate	2%
carboxymethyl cellulose	1%
kaolin	87%

The active ingredients are mixed with the additives, and the mixture is ground and moistened with water. This mixture is extruded, granulated and subsequently dried in a stream of air.

Example F9: Coated granulates

combination (1:1)	3%
polyethylene glycol (MW 200)	3%
kaolin	94%

In a mixer, the finely ground active ingredients are applied uniformly to kaolin, which has been moistened with polyethylene glycol, to give dust-free coated granules.

Example F10: Suspension concentrate

combination (2:1)	40%
ethylene glycol	10%
nonylphenol polyethoxylate (15 mol EO)	6%
sodium ligninsulfonate	10%
carboxymethyl cellulose	1%
37% aqueous formaldehyde solution	0.2%
silicone oil in the form of a 75% aqueous emulsion	0.8%
water	32%

The finely ground active ingredients are mixed intimately with the additives to give a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

It is often more expedient to formulate the compound of formula (I) and one of the 1-arylpyrazoles of formula (II) singly and then to mix them in the desired ratio in the applicator as a tank mixture in water shortly before application.

Biological Examples (% = per cent by weight, unless otherwise indicated)

A synergistic effect is always obtained whenever the activity of the combination of the compound of formula (I) with one of the pesticides (II) is greater than the sum of the activities of the individually applied compounds.

For example, the expected pesticidal activity We of a given combination of two pesticides can be calculated as follows (q.v. COLBY, S.R., "Calculating synergistic and antagonstic response of herbicide combinations". Weeds 15, pages 20-22, 1967):

$$We = X + \frac{Y \bullet (100 - X)}{100}$$

wherein

X = Percentage mortality, compared with untreated controls, after treatment with the compound of formula (I) at a rate of application of p g/hectare (= 0%).

Y = Percentage mortality, compared with untreated controls, after treatment with a arylpyrazole of formula (II) at a rate of application of q kg/hectare.

We = The expected pesticidal activity (percentage mortality compared with untreated controls) after treatment with the compound of formula (I) and a 1-arylpyrazole (II) at a rate of application of p + q kg a.i./ha.

If the actually observed value is greater than the expected value We, then there is synergism.

The synergistic effect of the combination of a compound of formula (I) with one of the 1-arylpyrazoles of formula (II) is demonstrated in the following non-limiting Examples.

Example 1: Action against Spodoptera Eridania

Artificial growth medium is treated with Compound C at rates of 0.5, 0.25, 0.125, 0.06, and 0.03 ppm. Artificial growth medium is treated with Compound A at rates of 8, 4, 2, 1 and 0.5 ppm. Artificial growth medium is treated with the following rate combinations of Compound C and Compound A: (0.5 + 8); (0.25 + 4); (0.125 + 2); (0.06 + 1); and (0.03 +0.5). Larvae of Spodoptera Eridania are placed in the medium and allowed to stay for days. Mortality is measured at 4 and 7 days after the larvae are allowed to begin to feed. The following results which show synergism in three of five rates are obtained at 4 days after treatment:

Rate (ppm)/% Mortality of Compound C	Rate (ppm)/% Mortality of fipronil	We	Actual Mortality of Compound C and fipronil
0.5 / 80	8 / 100	100	80
0.25 / 10	4 / 30	37	40
0.125 /10	2 / 0	10	40
0.06 / 10	1 / 10	19	30
0.03 / 0	0.5 / 0	0	0

The following results, which show synergy at two of the five rates, are obtained at 7 days after treatment (DAT).

Rate (ppm)/% Mortality of Compound C	Rate (ppm)/% Mortality of fipronil	We	Actual Mortality of Compound C and fipronil
0.5 / 100	8 / 100	100	100
0.25 / 100	4 / 70	100	100
0.125 / 80	2 / 40	88	100
0.06 / 80	1 / 30	86	100
0.03 / 0	0.5 / 20	20	20

This test illustrates the general synergism of the invention.

EXAMPLE 2

The procedure of Example 1 was followed using cotton leaves sprayed to runoff with combination using the rates shown in the following tables. The tables indicate individual data at the date after treatment indicated.

2 days after Treatment	
Rate (ppm)/% Mortality of Compound C	Rate (ppm)/% Mortality of Compound B
0.4 / 20	500 / 0
0.1 / 10	250 / 0
0.025 / 0	
0.006 / 0	
0.0015 / 0	

4 days after Treatment	
Rate (ppm)/% Mortality of Compound C	Rate (ppm)/% Mortality of Compound B
0.4 / 100	500 / 10
0.1 / 40	250 / 0
0.025 / 0	
0.006 / 0	
0.0015 / 0	

5 days after Treatment	
Rate (ppm)/% Mortality of Compound C	Rate (ppm)/% Mortality of Compound B
0.4 / 100	500 / 10
0.1 / 70	250 / 0
0.025 / 0	
0.006 / 0	
0.0015 / 0	

The following table indicates the results obtained with mixtures of Compound B and C.

Rate (ppm) Compound C	Rate (ppm) Compound B	We 2 DAT	Actual 2 DAT	We 4 DAT	Actual 4 DAT	We 5 DAT	Actual 5 DAT
0.4	500	40	20	100	100	100	100
0.1	500	10	0	46	60	77	100
0.025	500	0	0	10	20	10	30
0.006	500	0	0	10	0	10	10
0.0015	500	0	0	10	0	10	0
0.4	250	40	0	100	100	100	100
0.1	250	10	0	40	30	70	80
0.025	250	0	0	0	20	0	40
0.006	250	0	0	0	0	0	30
0.0015	250	0	0	0	0	0	0

EXAMPLE 3

In the test of Example 2, after five days, a general and substantial reduction in damage to the leaves is observed for the combination. Data for this test is shown in the following table:

Concentration of Compound C (ppm)	Concentration of Compound B (ppm)	Per cent Feeding Damage
0	0	60
0	250	60
0	500	50
0.4	0	2
0.1	0	10
0.025	0	60
0.006	0	60
0.0015	0	60
0.4	500	2
0.1	500	5
0.025	500	20
0.006	500	30
0.0015	500	60
0.4	250	2
0.1	250	5
0.025	250	25
0.006	250	30
0.0015	250	40

EXAMPLE 4

Cats, housed in cages with wire mesh bottoms, are infested with about 50 fleas at 1 week intervals for the course of the study. One day after the first infestation, the cats are treated by a subcutaneous injection of a mixture of Compound C at a rate of 10 mg/kg and Compound B at a rate of 20 mg/kg in polyethylene glycol. One day later, and two days after each weekly infestation for the course of the study, sweepings of debris which

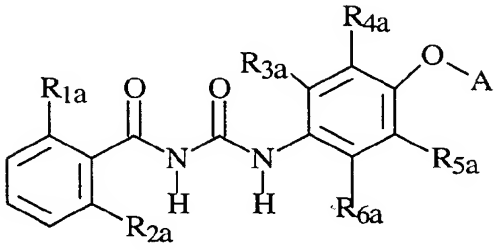
are collected on plywood boards placed beneath the cages are combined with flea rearing media and evaluated for development of flea progeny. Adult fleas on the cats are counted weekly, two days after each infestation, for the duration of the study by combing the cats. Greater than 95% control of development of flea progeny and >90% control of flea adults is maintained for 26 and 52 weeks post treatment.

EXAMPLE 5

Cats, housed in cages with wire mesh bottoms are infested with about 50 fleas at 1 week intervals for the course of the study. One day after the first infestation, the cats are treated by oral gavage via stomach tube of a mixture of Compound C at a rate of 20 mg/kg and Compound A at a rate of 20 mg/kg in a 1:1 v/v DMSO/corn oil mixture. One day later, and two days after each weekly infestation for the course of the study, sweepings of debris, which are collected on plywood boards placed beneath the cages, are combined with flea rearing media and evaluated for development of flea progeny. Adult fleas on the cats are counted weekly, two days after each infestation, for the duration of the study by combing the cats. Greater than 95% control of development of flea progeny and >90% control of flea adults is maintained for 26 and 52 weeks post treatment.

CLAIMS

1. A pesticidal combination comprising a compound of formula (I):



(I)

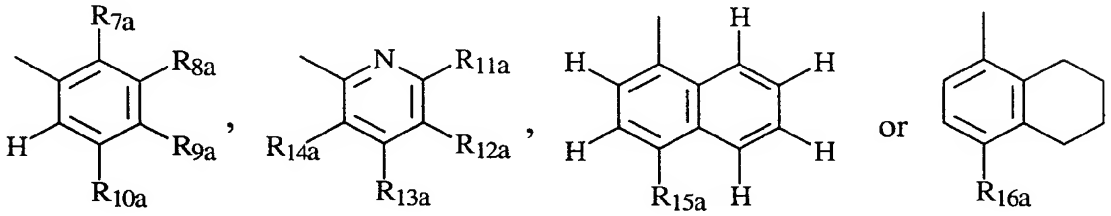
wherein:

R_{1a} and R_{2a} are independent of one another, hydrogen or halogen;

R_{3a} is hydrogen, chlorine or alkyl;

R_{4a}, R_{5a} and R_{6a} are independent of one another, alkyl, preferably methyl hydrogen, or halogen;

A is G1, G2, G3 or G4:

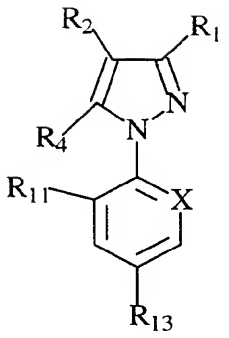


(G1) (G2) (G3) (G4)

wherein R_{7a} to R_{16a} are independent of one another, hydrogen, halogen, alkyl or nitro; and

provided that R_{1a} and R_{2a} are not simultaneously hydrogen; and that R_{4a}, R_{5a} and R_{6a} are not simultaneously hydrogen;

in the free form or in the form of a pesticidally acceptable salt thereof, and a 1-arylpyrazole of formula (II):



(II)

wherein:

R_1 is CN or methyl;

R_2 is $S(O)_nR_3$;

R_3 is alkyl or haloalkyl;

R_4 is selected from the group consisting of hydrogen, halogen, $-NR_5R_6$, $-C(O)OR_7$, $-S(O)_mR_7$, alkyl, haloalkyl, $-OR_8$, $-N=C(R_9)(R_{10})$ and -C(O)alkyl;

R_5 and R_6 are independently selected from a hydrogen atom, alkyl, haloalkyl, -C(O)alkyl, $-C(O)OR_7$, $-S(O)_rCF_3$; or R_5 and R_6 form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_7 is selected from alkyl and haloalkyl;

R_8 is selected from alkyl, haloalkyl and hydrogen;

R_9 is selected from hydrogen and alkyl;

R_{10} is selected from phenyl or heteroaryl each of which is optionally substituted by one or more hydroxy, halogen, -O-alkyl, -S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from nitrogen and C-R_{12};

R_{11} and R_{12} are independently selected from halogen or hydrogen;

R_{13} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_qCF_3$, $-SF_5$;

m, n, q, r are independently selected from 0, 1, and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2, R_{11} is Cl, R_{13} is CF_3, and X is N.

2. The combination according to claim 1 wherein the 1-arylpyrazoles of formula (II) are selected from a group of 1-arylpyrazoles with one or more of the following features:

R_1 is CN;

R_4 is $-NR_5R_6$;

R_5 and R_6 are independently selected from the hydrogen atom, alkyl, haloalkyl, C(O)alkyl, $C(O)OR_7$;

X is C-R_{12}; or

R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy, and $-SF_5$.

3. The combination according to any one of the foregoing claims wherein the 1-arylpyrazole of formula (II) is 5-amino-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile or 5-amino-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)-4-ethylsulfinylpyrazole-3-carbonitrile.

4. The combination according to any one of the foregoing claims which is long acting.

5. The combination according to any one of the foregoing claims which is synergistic.

6. The combination according to any one of the foregoing claims wherein the ratio of the compound of formula (I) and at least one 1-arylpyrazole is synergistic.

7. The combination according to any one of the foregoing claims which is an antifeedant.

8. A composition comprising a combination according to any one of claims 1-7 in association with a pesticidally acceptable adjuvant.

9. A method of controlling pests at a locus which comprises applying thereto a compound of formula (I) or a pesticidally acceptable salt thereof and a 1-arylpyrazole of formula (II).

10. The method according to claim 9 wherein the locus is an animal.

11. The method according to claim 9 or claim 10 wherein the combination is applied orally.

12. The method according to any one of claims 9 to 11 wherein the combination is applied by a subcutaneous injection or implant.

13. A product comprising a compound of formula (I) in its free form or a pesticidally acceptable salt thereof and a 1-arylpyrazole of formula (II) for simultaneous, separate or sequential use in the control of pests at a locus.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 98/01224

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N47/02 A01N43/56 A61K31/415 //(A01N47/02,47:34), (A01N43/56,47:34),(A61K31/415,31:17)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 713 889 A (SUMITOMO CHEMICAL CO) 23 June 1995 see page 1, line 1 - page 2, line 14 see page 3, line 24 - line 26 see page 4, line 15 - page 5, line 19	1-9,13
Y	see page 3, line 19 - page 4, line 7 ---	1-13
Y	EP 0 295 117 A (MAY & BAKER LTD) 14 December 1988 see page 2, line 5 - line 29 see page 3, line 46 see page 4, line 42 - page 5, line 42 see page 5, line 65 see page 6, line 17 - line 23 see page 7, line 64 - line 65 see page 8, line 3 --- -/--	1-13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 July 1998	13/07/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Lamers, W

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 98/01224

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 86 05780 A (UNION CARBIDE CORP) 9 October 1986 see page 1, paragraph 2 see page 2, line 17 - line 18 see page 5; table A see page 35, paragraph 4 - page 36, paragraph 1 see claim 23	1-9,13
Y	WO 86 03941 A (UNION CARBIDE CORP) 17 July 1986 see page 1, paragraph 2 see page 113, paragraph 1 - page 118, paragraph 3 see page 146; example 15	10-12
P,X	DE 195 48 874 A (BAYER AG) 3 July 1997 see page 2, line 3 - page 3, line 23	1-9,13
P,X	WO 97 36485 A (MERIAL) 9 October 1997 see page 2, line 35 - page 6, line 26 see page 7, line 4 see page 7, line 7 see page 7, line 32 - page 9, line 17	1-10,13
A	WO 95 33380 A (CIBA GEIGY AG ;SKILLMAN STEPHEN WILSON (CH); BUHOLZER FRANZ (CH)) 14 December 1995 see page 1, paragraph 3 see page 4, line 23 - line 25	1-13
A	EP 0 255 803 A (CIBA GEIGY AG) 10 February 1988 see page 3, line 41 - line 47 see page 8, line 11 - line 36	1-13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/EP 98/01224

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2713889 A	23-06-1995	JP 7179307 A	18-07-1995
		BR 9405197 A	17-10-1995
		CN 1124087 A	12-06-1996
		ES 2100122 A	01-06-1997
		IT RM940820 A,B	21-06-1995
		US 5567429 A	22-10-1996
EP 0295117 A	14-12-1988	AU 618266 B	19-12-1991
		AU 1755488 A	15-12-1988
		CA 1330089 A	07-06-1994
		CN 1027341 B	11-01-1995
		DD 281744 B	20-02-1997
		DK 314088 A	13-12-1988
		EG 19113 A	30-11-1994
		FI 882735 A	13-12-1988
		FI 951839 A	18-04-1995
		HU 210668 B	28-06-1995
		HU 9500470 A	30-10-1995
		IL 105138 A	26-08-1994
		JP 2669538 B	29-10-1997
		JP 63316771 A	26-12-1988
		KR 9701475 B	06-02-1997
		MX 11842 A	01-12-1993
		NO 175367 B	27-06-1994
		OA 8880 A	31-10-1989
		PH 26895 A	03-12-1992
		PT 87697 B	30-09-1992
		RO 106496 A	31-05-1993
		RU 2051909 C	10-01-1996
		US 5547974 A	20-08-1996
		US 5714191 A	03-02-1998
		US 5608077 A	04-03-1997
		US 5232940 A	03-08-1993
WO 8605780 A	09-10-1986	AP 9 A	18-12-1987
		AU 585002 B	08-06-1989
		AU 5583486 A	23-10-1986
		BR 8606564 A	04-08-1987
		CS 8602217 A	16-09-1988
		DE 3661195 A	22-12-1988

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter onal Application No
PCT/EP 98/01224

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8605780 A		DK 573586 A	28-01-1987
		EP 0215841 A	01-04-1987
		FI 864872 A	28-11-1986
		JP 62502335 T	10-09-1987
		OA 8493 A	29-07-1988
		US 4880838 A	14-11-1989
WO 8603941 A	17-07-1986	US 5135953 A	04-08-1992
		AU 599313 B	19-07-1990
		AU 5300686 A	29-07-1986
		BR 8507149 A	31-03-1987
		DK 408286 A	17-10-1986
		EP 0211004 A	25-02-1987
		FI 863490 A	28-08-1986
		OA 8537 A	30-09-1988
		PT 81768 B	02-10-1987
		US 5420163 A	30-05-1995
DE 19548874 A	03-07-1997	NONE	
WO 9736485 A	09-10-1997	FR 2746594 A	03-10-1997
		AU 2512997 A	22-10-1997
		DE 19780440 T	20-05-1998
		DK 136497 A	29-01-1998
		FI 974351 A	27-11-1997
		FR 2746597 A	03-10-1997
		GB 2317564 A	01-04-1998
		LU 90176 A	27-01-1998
		NL 1005676 C	30-09-1997
		NO 975472 A	29-01-1998
		PL 323604 A	14-04-1998
		SE 9704304 A	24-11-1997
WO 9533380 A	14-12-1995	AU 2616695 A	04-01-1996
		BR 9502710 A	09-04-1996
		CN 1150381 A	21-05-1997
		EP 0765120 A	02-04-1997
		JP 10502055 T	24-02-1998
		ZA 9504683 A	08-12-1995

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ɔnal Application No
PCT/EP 98/01224

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0255803 A	10-02-1988	AU 606349 B	07-02-1991
		AU 7658187 A	11-02-1988
		DK 408587 A	07-02-1988
		FI 873357 A	07-02-1988
		JP 63072631 A	02-04-1988
		PT 85475 B	08-02-1991
		US 5416102 A	16-05-1995
		US 4973589 A	27-11-1990
		ZA 8705776 A	08-02-1988